REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
02-12-2008	Final Report	1-Oct-2005 - 30-Sep-2008

4. TITLE AND SUBTITLE
Final Report on Responsive Polymer Surfaces Project

5a. CONTRACT NUMBER
W911NF-05-1-0559

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
Alfred J. Crosby

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Massachusetts - Amherst
Office of Grant & Contract Admin.
408 Goodell Building
Amherst, MA 01003 -3285

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
48705-MS.1

12. DISTRIBUTION AVAILIBILITY STATEMENT Approved for Public Release; Federal Purpose Rights
Distribution authorized to U.S. Government Agencies Only; Contains Proprietary information

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
This project focused on the fabrication and characterization of responsive polymer interfaces to be used as "smart" coatings that dynamically alter surface properties, advanced optical devices, and/or sensors. Transition speed, magnitude of change, and sensitivity are primary challenges in the development of responsive surfaces. To meet these challenges, we developed polymer surfaces with controlled shell structures that transition via snap-through or crumpling elastic instabilities upon the application of a trigger. During this final reporting period, we have focused on three primary aspects of these responsive surface-attached shells: 1) the dynamics of snap; 2) the adhesion of crumpling surface structures; and 3) the crumpling of

15. SUBJECT TERMS
polymer surfaces, mechanical instabilities, responsive surfaces, adhesion, snapping, elastomers, patterned surfaces

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Alfred Crosby
U	U	U	SAR		19b. TELEPHONE NUMBER 413-577-1313

Report Title

Final Report on Responsive Polymer Surfaces Project

ABSTRACT

This project focused on the fabrication and characterization of responsive polymer interfaces to be used as "smart" coatings that dynamically alter surface properties, advanced optical devices, and/or sensors. Transition speed, magnitude of change, and sensitivity are primary challenges in the development of responsive surfaces. To meet these challenges, we developed polymer surfaces with controlled shell structures that transition via snap-through or crumpling elastic instabilities upon the application of a trigger. During this final reporting period, we have focused on three primary aspects of these responsive surface-attached shells: 1) the dynamics of snap; 2) the adhesion of crumpling surface structures; and 3) the crumpling of ultrathin polymer films for the fabrication of sub-micron surface patterns. In addition to the three papers related to this project published in significant peer-review journals, we are currently preparing three manuscripts to publish the results of each of the three focused initiatives of this past funding period. Several presentations on this research also have been delivered at national and international symposia, a full patent for the developed technology has been filed, companies and private investors have expressed interest in this technology, and the research has received numerous highlights in the national and local media.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Kyriaki Kalaitzidou , Alfred J. Crosby. “Adaptive Polymer Particles.” Applied Physics Letters, 2008, 93, 4, 041910.

Douglas Holmes, Michal Ursiny, Alfred J. Crosby. “Crumpled Surface Structures.” Soft Matter, 2008, 4, 82-85.

Douglas Holmes and Alfred J. Crosby. “Snapping Surfaces” Advanced Materials, 2007, 19, 3589-3593.

Number of Papers published in peer-reviewed journals: 3.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Douglas Holmes, Derek Breid, Edwin P. Chan, Alfred J. Crosby. “Wrinkling and Snapping Polymer Surfaces.” ACS Spring Meeting: PMSE Preprints, New Orleans, LA, 2008.

Douglas Holmes, Derek Breid, Edwin P. Chan, Alfred J. Crosby. “Responsive Polymer Surfaces.” Proc. Of the 31st Ann. Conf. Adh. Soc., 2008.

Number of Papers published in non peer-reviewed journals: 2.00

(c) Presentations

18. “Wrinkling, Crumpling, and Snapping for Surface Property Control.” Korean Polymer Society Fall Conference, Seoul, S. Korea, October 2008. (invited)

17. “Wrinkling, Crumpling, and Snapping for Surface Property Control.” Seoul National University Chemical Engineering Seminar, Seoul, S. Korea, October 2008. (invited)

16. “Wrinkling, Crumpling, and Snapping for Surface Property Control.” KAIST Chemical Engineering Seminar, Daejeon, S. Korea, October 2008. (invited)

15. “Wrinkling, Crumpling, and Snapping for Surface Property Control.” POSTECH Chemical Engineering Seminar, Pohang, S. Korea, October 2008. (invited)

14. “Wrinkling, Crumpling, and Snapping for Surface Property Control.” MIT Physical Mathematics Seminar, Boston, MA, September 2008. (invited)

13. “Wrinkling and Crumpling for Surface Property Control” POLYFilm Conference, University of Sheffield, UK, September 2008. (invited)

12. “Wrinkling, Crumpling, and Snapping Polymer Surfaces” US-Korea Conference on Science, Technology, and Entrepreneurship, San Diego, CA August 2008. (invited)

11. “Lessons from a Fingerprint, Literally” Gordon Research Conference Polymer Physics, Newport, RI, June 2008. (invited)

10. “Listening to Materials Respond: New Lessons for Soft Materials Design” Rohm & Haas Corporation Electronic Materials Seminar Series, Marlboro, MA, June 2008. (invited)

9. “Wrinkling, Crumpling, and Snapping Polymer Surfaces” Rohm & Haas Corporation Technical Seminar Series, Spring House, PA, May 2008. (invited)

8. “Wrinkling, Crumpling, and Snapping Polymer Surfaces” Dow Corning Corporation Seminar Series, Midland, MI, May 2008. (invited)

7. “Wrinkling, Crumpling, and Snapping Polymer Surfaces” American Chemical Society Rubber Division Technical Meeting, Dearborn, MI, April 2008. (invited)

6. “Wrinkling, Crumpling, and Snapping Polymer Surfaces” Proctor & Gamble NanoSeries, Cincinnati, OH, March 2008. (invited)

5. “Wrinkling, Crumpling, and Snapping for Surface Property Control” American Physical Society March Meeting, Division of Polymer Physics, New Orleans, LA, March 2008. (invited)

4. “Wrinkling, Crumpling, and Snapping Polymer Surfaces” Saint Gobain Seminar, Northboro, MA, March 2008. (invited)

3. “Interfacial Control: Using the Laws of Nature.” Adhesives and Sealants Council Executive Meeting, Austin, TX, February 2008. (invited)

2. “Mechanics of Hierarchical Materials.” Beijing University of Chemical Technology, Beijing, China, October 2007. (invited)

1. “Nature’s Instabilities: Inspiring Materials Design and Characterization.” Cellular and Molecular Medicine Seminar Series, University of Ottawa, October 2007. (invited)

Number of Presentations: 18.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Douglas Holmes	1.00
Chelsea Davis	0.00
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Kyriaki Kalaitzidou	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Alfred J. Crosby	0.08	No
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

5 **Snapping Surfaces for Sensors and Adhesion Control**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Alfred J. Crosby

5f-1a: University of Massachusetts Amherst

5f-c: 120 Governors Drive

Amherst MA 01003

5a: Douglas Holmes

5f-1a: University of Massachusetts Amherst

5f-c: 120 Governors Drive

Amherst MA 01003

5a: Kyriaki Kalaitzidou

5f-1a: University of Massachusetts Amherst

5f-c: 120 Governors Drive

Amherst MA 01003

5a: Charles Rand

5f-1a: University of Massachusetts Amherst

5f-c: 120 Governors Drive

Amherst MA 01003

5a: Edwin P. Chan

5f-1a: University of Massachusetts Amherst

5f-c: 120 Governors Drive

Amherst MA 01003

Responsive Polymer Interfaces

Alfred J. Crosby
Polymer Science & Engineering Department
University of Massachusetts Amherst
Fall 2008

Overview

Several strategies for surface patterning from photolithography to block copolymer self-assembly have been developed over the last several decades. Although these strategies are robust, many current and future applications will be enhanced significantly by the incorporation of surface patterns that adapt to their environment or change upon command. This project focused on the fabrication and characterization of such surfaces, which will be used as "smart" coatings that dynamically alter surface properties, advanced optical devices, and/or sensors. Our primary strategy was based on the development of polymer surfaces with controlled shell structures that transition via snap-through or crumpling elastic instabilities upon the application of a trigger. During this final reporting period, we have focused on three primary aspects of these responsive surface-attached shells: 1) the dynamics of snap; 2) the adhesion of crumpling surface structures; and 3) the crumpling of ultrathin polymer films for the fabrication of sub-micron surface patterns.

Dynamics of Snapping Surfaces

We have previously presented surfaces with microstructures that change topography over a very large lateral length scale and very short timescale by transitioning through a snap-buckling elastic instability. From the continuum mechanics of shell structures, it is known that at a critical applied stress an elastic instability will occur, similar to the Euler buckling of a beam. A complete description of the shell mechanics for the snap-through instability has not yet been accomplished. Therefore, further understanding of the balance between material properties and geometry to the critical stress is necessary to properly tune and design snapping surfaces. To study this phenomenon, we are controlled the internally applied pressure of an individual shell and measured the snap-through process optically (Figure 1). Internal pressure variation is advantageous because it is a reversible trigger and can be applied at various rates to determine the sensitivity of the elastic instability. The materials system consists of PDMS shells on a PDMS substrate and the shell thickness, t, radius, a, and applied strain were varied to determine the impact of geometry on the critical snap-through stress. These experiments allow us to determine the effect of geometry on the critical stress and sensitivity of these surfaces, which is essential for the development of the next generation of responsive materials.

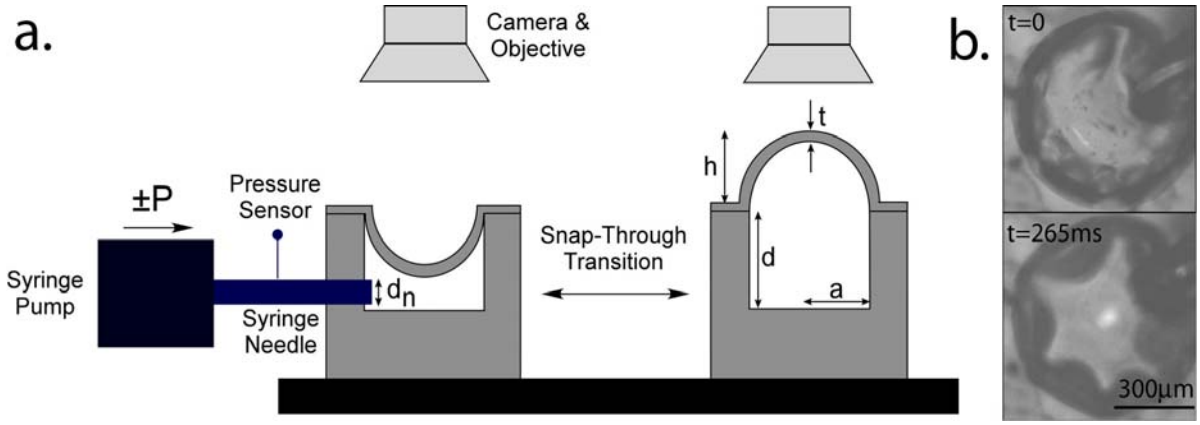

Figure 1 a. A schematic of the applied pressure and pressure sensor used to trigger the snap-through instability that is observed optically. b. Optical micrographs of the snap-through of an individual shell at a critical applied stress. Time difference between top and bottom images is 265ms.

Adhesion of Crumpling Surface Features

As reported in the interim report in 2007, an alternative approach for inducing responsive pattern transformations is the use of secondary bifurcation events in surface-attached shells. We refer to these transitions as the initial stages of crumpling. Structures that demonstrate these concepts are fabricated by placing a patterned PDMS substrate under equibiaxial strain through inflation and then bonding a capping layer to the patterned depressions. Upon release of the equibiaxial strain, the capping layer buckles above each of the patterned depressions to create a surface array of shell structures, whose geometry is dictated by the magnitude of applied processing strain. Higher strains lead to the generation of higher aspect ratio features. (Figure 3) By changing strain through environmental triggers, the microstructures can dynamically change their shape.

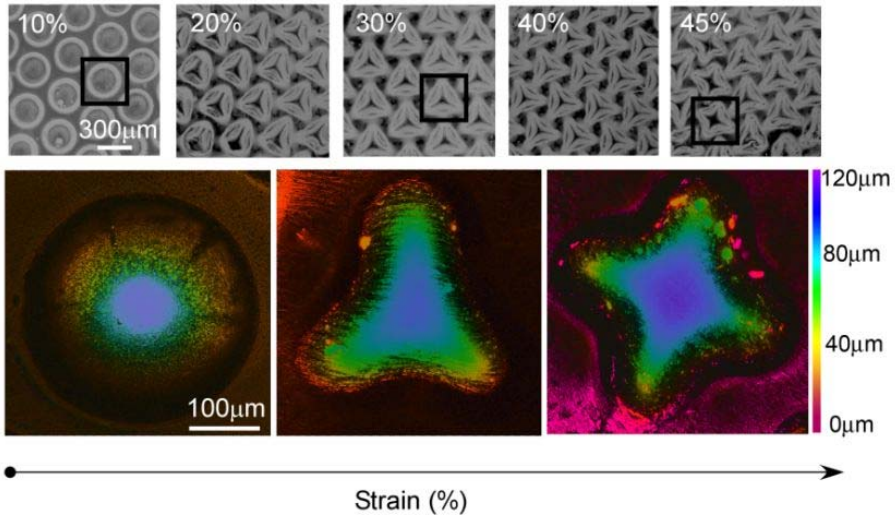

Figure 2. Top: Optical micrographs of fabricated shell structures. Bottom: Confocal microscope images of individual buckled shells, demonstrating change in feature geometry as a function of applied processing strain.

These transformations of secondary bifurcation provide a fast, robust, and sensitive approach for creating coatings that can dynamically alter their adhesion. To quantitatively measure the change in adhesion as a function of crumpled shell geometry, we have used contact mechanics-based adhesion measurements on custom-built instrumentation to quantify the force-displacement-contact area relationship during contact and separation. Figure 4 shows the change in the maximum separation stress as a function of processing strain, which correspond to the interfacial area changes shown in the accompanying images. As measured, the dynamic response of these surface-attached shell features provides a mechanism for altering the separation stress of an elastomer/glass interface by nearly three orders of magnitude. This change in adhesion is significant and can be applied to variety of applications, including anti-fouling coatings.

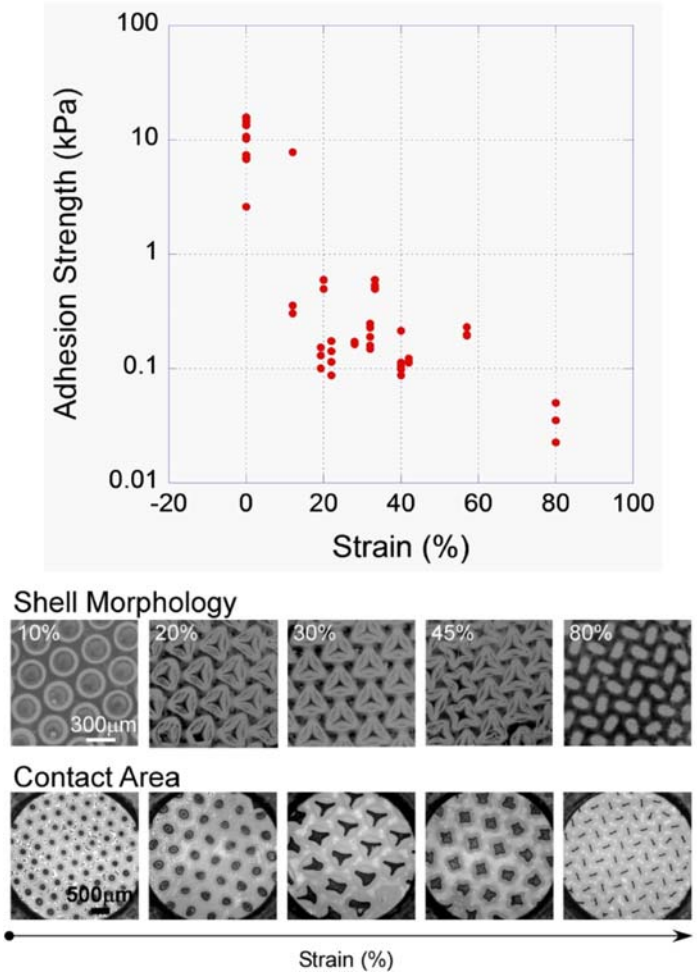

Figure 3. Maximum separation stress, or adhesion strength, for polydimethylsiloxane surface-attached shell structures separating from a flat, fused silica cylindrical punch at a controlled velocity. Strain refers to fabrication strain, which alters the morphology of surface-attached shell structures as shown in images. Images of maximum contact area between shell structures and fused silica surface are shown in bottom row.

In a related effort during this final reporting period, we conducted a simple experiment to demonstrate the potential for snapping surface transitions as effective coating release mechanisms. The experiment consisted of applying a thin coating of a poly(methyl methacrylate) (PMMA) latex, i.e. paint, on a surface of concave shell structures. After drying, the shell structures were snapped from concave to convex structures triggered by a change in the relative air pressure. This transition caused the shell structures to induce extensive fracturing in the latex coating, which could subsequently be removed in a straightforward manner. This simple demonstration is confirmation of one of the initial application ideas that was proposed in the original project proposal.

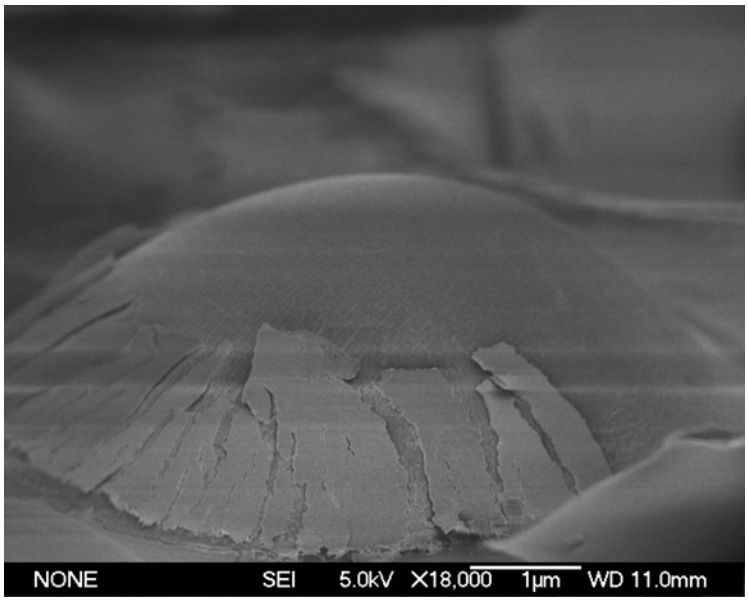

Figure 4. SEM micrograph of fractured PMMA latex film on surface of PDMS shell, which transitioned from concave to convex upon triggering. Demonstrates concept of on-command release of protective coatings, such as paint.

Crumpled Thin Films

Most recently, our efforts have focused on developing and investigating sub-micron responsive structures. Our initial work has focused on the crumpling and folding of a sub-micron polymer film that delaminates from a rigid substrate. Consider a thin, unstrained film of polystyrene attached to a strained silicon substrate. Upon releasing the strain in the substrate, the polystyrene film delaminates at localized regions as dictated by the balance of mechanical strain energy and adhesion strength of the polystyrene-silicon interface. In the delaminated regions, the polystyrene film localizes its strain energy into sharp curvatures, or folds. The sharp structure of crumpling occurs because of the film's preference to bend instead of stretch. The lack of stretching causes the film to respond to an applied force by making deformations confined to small regions of the film. The result is that strain is localized at a ridge of bent material that makes up the crumpled surface (Figure 1). To fabricate these folds in polymer thin films, we use the uniaxial compression of an elastic substrate. The substrate is either crosslinked polydimethylsiloxane (PDMS) or a silicon wafer, and the thin polymer film is polystyrene (PS), though the process could be extended to a variety

of materials. The PDMS substrate is exposed to ultraviolet light in the presence of ozone (UVO) which creates a SiO_X layer on the surface (PDMS-U), and decreases the adhesion between the PS and the substrate. The substrate is placed in uniaxial tension and brought into contact with a floating PS film. The release of the substrate generates a uniaxial compressive stress, and upon exceeding a critical value, the PS film delaminates from the substrate surface. (Figure 5). We've demonstrated folding of films down to 5nm in thickness with aspect ratios (height/width) near unity, lateral dimensions of ~100 nm, and lengths of several microns. The width of these structures can be tuned by varying either the film thickness or applied strain (Figure 5). Features on these length scales provide fresh opportunities for developing responsive structures on sub-micron length scales in a scalable, robust manner.

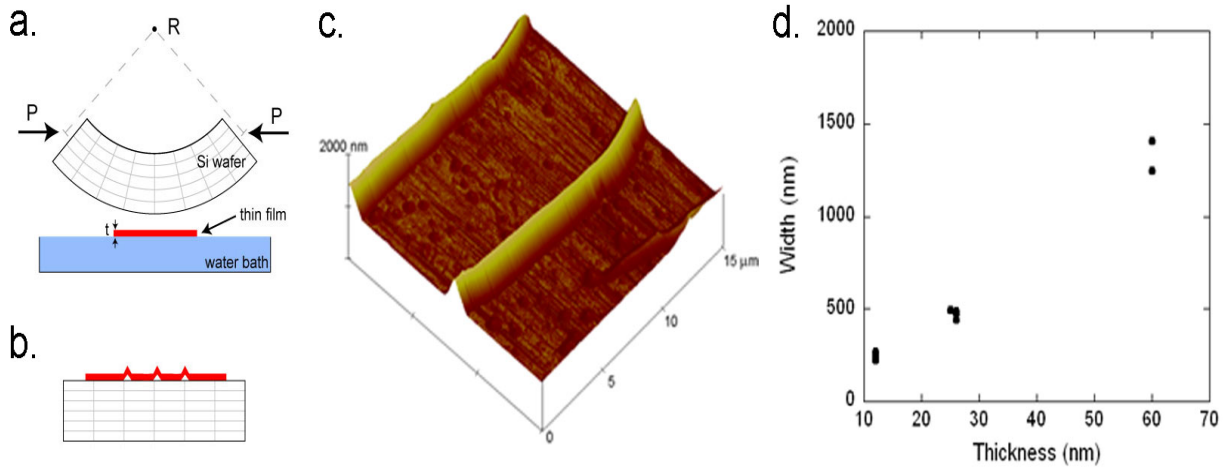

Figure 5 A schematic showing the fabrication process: a. the attachment of a thin polymer film to a bent silicon wafer. b. The resultant crumpled surface upon release of the compressed wafer. c. An AFM micrograph of polystyrene folds aligned perpendicular to the applied uniaxial compressive stress. d. A plot of fold width vs. film thickness, showing preliminary data that allows us to predict feature width.

Impact through Publications and Presentations

In addition to the three papers related to this project published in significant peer-review journals, we are currently preparing three manuscripts to publish the results of each of the three focused initiatives of this past funding period. Several presentations on this research also have been delivered at national and international symposia, a full patent for the developed technology has been filed, companies and private investors have expressed interest in this technology, and the research has received numerous highlights in the national and local media.